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DIFFUSION COLORATION OF INDUSTRIAL THERMALLY POLISHED GLASS WITH SOLID-PHASE COPPER-CONTAINING REAGENTS

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The process for obtaining coloring of the “copper ruby” type in thermochemical treatment of thermally polished glass with copper-containing reagents was examined. Data are reported on the effect of the compositions of the working solutions and process regimes on the character of the coloring and the spectral characteristics of the glasses. Formation of the diffusion layer and the effect of different factors on the quality of the “copper ruby” obtained were investigated, and practical recommendations were given on selecting the optimum coloring regimes.

Thermally polished glass, or float glass, is attracting the attention of researchers due to the reducing properties of its surface in contact with the tin melt during formation. According to the data in [1, 2], the tin is in several charge states — Sn^0, Sn^{2+}, Sn^{4+}, and less oxidized forms are located in the surface layers. The efficacy of diffusion coloring of thermally polished glass in copper(I) chloride vapors and melt and making colored glass filters with intense absorption in the range of wavelengths up to 570 nm was demonstrated previously [3, 4]. However, the use of salt melts as the modifying medium has many drawbacks and limitations, including the long duration of thermochemical processing and technical difficulties in organizing production of colored glasses.

All of this has stimulated a search for new ways of conducting the process, in particular, using ion-exchange reagents in the form of solutions applied on the surface of the glass by the aerosol method. This technology is used for ion-exchange strengthening of glass with potassium salts [5]. The essence of the process of treatment with a solid-phase reagent consists of the following: Solutions of reagents are applied to the surface of the glass at high temperatures (higher than the glass transition temperature t_g) by spraying and after evaporation of the solvent, a solid layer of the reagent forms on the glass. The glass with the solid phase layer is then held in a furnace to continue the diffusion process. After cooling, the surface of the glass is washed to remove the remaining film of reagent.

We investigated selection of copper-containing reagents, optimization of the compositions of the working solutions for aerosol treatment, and the effect of the thermochemical treatment regimes on diffusion coloring of glass.

The chemical composition and concentration of the solution are important for optimizing formation of a solid-phase layer of copper containing reagent in the glass. The copper compounds were selected based on the following requirements: nontoxicity, availability, good solubility in water or other noncombustible solvents, and low tendency toward thermohydrolysis with formation of oxide coatings. For this reason, copper(I) and (II) chlorides and copper(II) sulfate pentahydrate were selected. Since copper(I) chloride has low solubility in water, a 25% ammonia solution was also used as the solvent. In preparing the solutions, we found that the solubility of copper(I) chloride in a solution of ammonia is low at room temperature and solutions with a sufficient concentration could only be obtained if zinc salts were added to the solution. The Zn^{2+} cation, which is a good complexing agent, dissolves copper(I) chloride.

The modifying layer on the surface of the glass was obtained on a laboratory setup by spraying the solutions onto a heated glass support. The instrument in the setup allows regulating the basic process spraying parameters within relatively wide limits: the position and distance of the nozzle to the glass samples (50 – 80 cm), medium spraying pressure (0.1 – 0.4 MPa), degree of dispersion of the aerosol, spraying temperature and duration.

Diffusion coloring of glass by the aerosol method consisted of the following stages:

heating the glass in the unit;

spraying the solution on the surface of the glass;

holding the glass with the reagent layer in the chamber of the unit;

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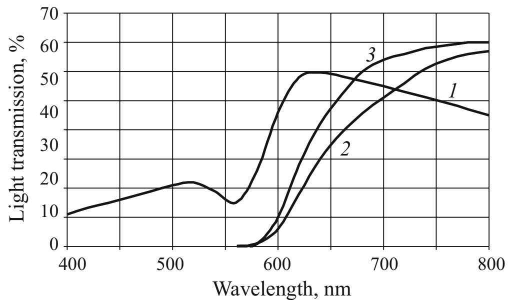

Fig. 1. Spectral transmission of float glass treated with heat at 650°C with an aqueous solution of $CuCl_2$ (*1*), and ammonia solutions of $CuSO_4$ (*2*) and CuCl (*3*).

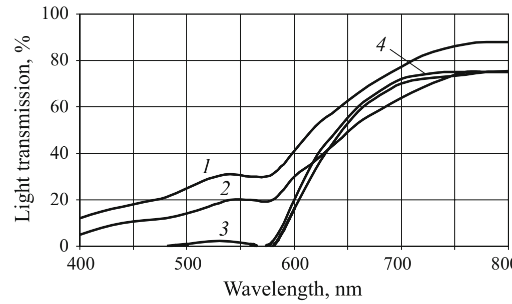

Fig. 2. Spectral transmission of float glass treated with heat at 650°C with ammonia solutions of CuCl with $Zn(NO_3)_2$ (*1*), $ZnCl_2$ (*2*), $ZnSO_4$ (*3*), and $Zn_3(PO_4)_2$ additives (*4*).

heat treating the glass with the reagent layer in an annealing furnace;

cooling the glass and removing the reagent film.

As a result of thermochemical treatment with copper-containing solutions, the surface of the glass acquired red coloring of varying intensity. A visual evaluation of the samples showed that the quality of the coloring was determined by the composition of the copper-containing solutions. In spraying an aqueous solution of copper(II) chloride, the glass was unevenly colored red-orange, while the aqueous solution of copper(II) sulfate turned the glass bright red, but the color was also not uniform. Use of ammonia solutions of copper(II) sulfate and copper(I) chloride with zinc salt additives resulted in more uniform coloring. A study of the surface morphology of the colored glass using a petrographic computer package in transmitted light showed that in the case of aqueous solutions, the surface consisted of colored and uncolored sections with a different degree of inhomogeneity. When ammonia solutions were used, the surface became more homogeneous and uniformly colored. When aqueous solutions were used, the necessary degree of contact of the solid layer of reagent and the surface of the glass was probably not attained. In addition, use of an ammonia solution as the solvent had a milder effect on the surface of the glass.

The quality of the ruby color is higher the more it passes red rays and the more strongly it absorbs blue and green rays. Since the copper ruby absorption curve is very constant, the color quality can be assessed with the ratio of the densities at maximum and minimum transmission, in our case, the ratio of wavelengths $D_{\lambda = 570 \text{ nm}}/D_{\lambda = 750 \text{ nm}}$. For good quality ruby, this ratio should be ≥ 7. The spectral transmission curves (Fig. 1) show that quality coloring is only attained when solutions of copper sulfate and copper (I) chloride with additives are used.

Further studies showed that zinc compound additives not only caused dissolution of copper(I) chloride in ammonia but also affected the diffusion coloring process. There are published data on the enhancing role of zinc compounds in ion-exchange coloring of glass (British Patent No. 917388), where Zn^{2+} ions increase the diffusion rate of reduced metal ions. We investigated zinc chloride, sulfate, carbonate, nitrate, and phosphate additives. The spectral transmission curves of the colored glasses (Fig. 2) show that the best results were obtained with zinc phosphate and sulfate. The effect of the anionic constituent acted both in the stage of preparation of the solution (different concentrations of additives) and in the stage of formation of the reagent layer.

Three compositions of solutions for aerosol treatment of glass were selected based on these studies: copper containing components — $CuSO_4$, CuCl; additives — $Zn_3(PO_4)_2$, $ZnSO_4$; solvent — 25% solution of NH_3, and the optimum concentrations of the basic component and additives were determined.

To optimize the thermochemical treatment regime, we investigated the effect of each stage of the process on the spectral characteristics of the colored glasses.

Preliminary heating of the glass to the process temperature in the sprayer chamber is necessary for rapid formation and fixation of the reagent layer on the surface of the glass and for intensifying the initial stage of ion diffusion. In addition, heating the glass keeps it from cracking in reacting with the cold reagent solution. The heating time is a function of the process temperature and thickness of the glass and is 1.5 – 3 min.

Spraying aerosol and holding in the chamber. These parameters are related, considering the diffusion coloring stage [4]: diffusion of copper(I) and (II) ions from the contact layer to the surface of the glass due to removal of sodium ions from it; reduction of copper ions to the metallic state; diffusion of Cu^0 particles in the glass with formation of particles of colloidal size.

The temperature of spraying the aerosol and holding the sample with the reagent layer in the furnace determines the rate of the diffusion processes in the glass and the intensity of reduction of copper ions to the atomic state. The solution spraying time ensures the required thickness of the reagent layer and is combined with holding in the heated chamber of the unit with the reagent layer necessary for the appearance of color, i.e., for diffusion of Cu^0 atoms in the glass and aggregation to particles of colloidal size. The temperature of applying the aerosol and holding in the unit varied within the range of 600 – 750°C, spraying time of 3 – 20 sec, and holding time of 1 – 3 min.

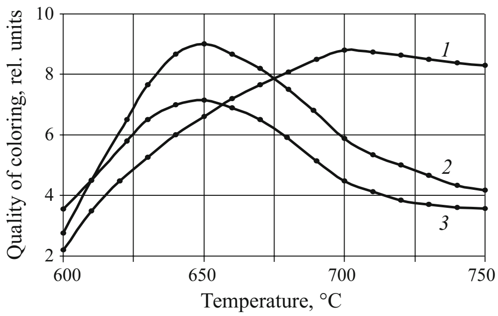

Fig. 3. Effect of the temperature of treatment with the copper-containing reagent on the coloring quality ($D_{\lambda = 570\text{ nm}}/D_{\lambda = 750\text{ nm}}$) in holding for 1 min (*1*), 2 min (*2*), and 3 min (*3*).

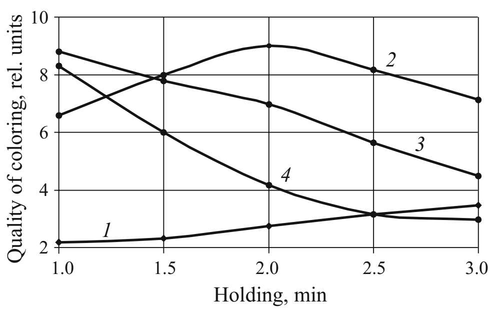

Fig. 4. Effect of the holding time with the reagent layer on the quality of coloring ($D_{\lambda = 570\text{ nm}}/D_{\lambda = 750\text{ nm}}$) at application temperatures of 600°C (*1*), 650°C (*2*), 700°C (*3*), and 750°C (*4*).

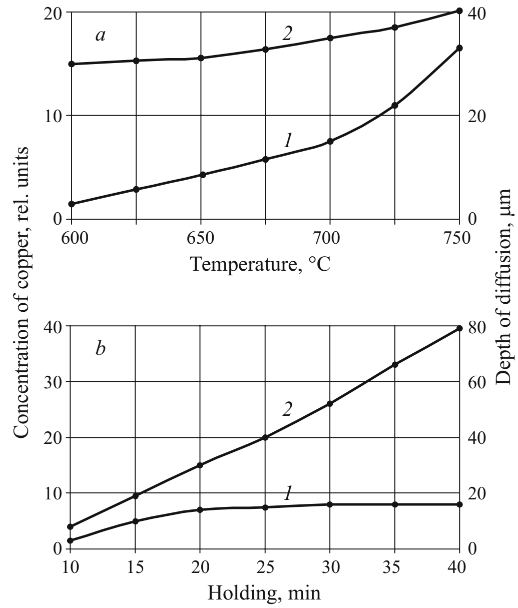

Fig. 5. Change in the concentration of copper in the surface layer (*1*) and thickness of the diffusion layer (*2*) as a function of the temperature of aerosol treatment of the copper-containing reagent (*a*) and the holding time with the reagent layer (*b*).

The studies showed that the optimum layer of reagent (of the order of 0.5 mm) was formed in 5 sec, as longer spraying of the cold solution significantly reduced the temperature in the spraying chamber and caused unnecessary consumption of the reagent. The curves in Figs. 3 and 4 show that when the process temperature increased, the holding time for obtaining high-quality coloring decreased. At 600°C, high-quality color was not obtained even with maximum holding. When the temperature was increased to 650°C and higher, high-quality color was obtained in 2 – 3 min. At high temperatures (700 – 750°C), increasing the duration of the process above 1 min worsened the quality of the ruby.

As a result of analyzing the spectral transmission and absorption curves, we found that increasing the temperature and holding time decreased transmission in the red region of the spectrum, and the optical density at the wavelength of 570 nm changed insignificantly. The study of the surface morphology of the colored glasses showed that a dull coating appeared on the surface at high temperatures and this decreased the overall light transmission.

The best quality of ruby color with a homogeneous surface microstructure was thus obtained in spraying aerosol at the temperature of 650°C for 5 sec and then holding for 2 – 3 min.

The depth of penetration of the copper into the glass and concentration in the surface layer was investigated by micro-x-ray-spectral analysis. The concentration of copper in the surface layer of the glass increased with an increase in the temperature, while the thickness of the diffusion layer changed insignificantly (Fig. 5*a*).

Additional heat treatment was conducted in the annealing furnace in the 450 – 500°C range for 0.5 – 1 h. When the glass was strengthened with a solid-phase reagent, potassium ions diffused into the surface layers of the glass and compressive stresses formed in this period. The additional treatment did not significantly affect the spectral characteristics of the colored glasses. The data in Fig. 5*b* show that copper diffused into the deep layers of the glass on additional holding of glass with a reagent layer, while the concentration of copper did not change after 15 min of treatment.

It is thus not so much the maximum depth of diffusion of copper into the glass as the concentration of colloidal particles in the surface layer that affects regulation of spectral transmission. We also know that the intensity of the color of rubies is not determined by the number of colloidal copper particles but by their size, which is usually a function of the deposition temperature. As a consequence, in diffusion coloring of glass with solid-phase, copper-containing reagents to obtain color of the “copper ruby” type, the temperature of spraying the aerosol and holding with the reagent layer acquires primary importance. The saturation of the surface layers of the glass with copper ions increases at high temperatures, their reduction rate increases, and the colloidal particles separated grow. The holding time with the reagent layer is a dependent value. The stage of annealing with the reagent layer does not significantly affect the spectral characteristics

of the colored glass and can be eliminated from the manufacturing process.

This technology for coloring float glass with solid-phase copper-containing reagents was successfully tested on units for application of oxide-metal coatings at Suksunskii Optical-Mechanical Plant and Institute of Class (GIS) pilot plant.

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